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Polymerizable Derivatives of Long-Chain Fatty Acids. VII.* Copolymerization of Vinyl Acetate with Some Long-Chain Vinyl Esters†

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INTRODUCTION

Little work has been reported on the copolymerization of vinyl esters of the long-chain fatty acids with vinyl acetate. Fikentscher² mentioned that vinyl methylvalerate and vinyl acetate in 1:1 ratio copolymerized to give a clear film which flows. Reppe *et al.*³ obtained insoluble products by the bulk copolymerization of vinyl acetate with vinyl oleate and also with vinyl palmitate, and a soluble product from vinyl chloroacetate and vinyl stearate by solution copolymerization. In neither publication is there described the preparation or purification of copolymers over a range of compositions, proof of copolymerization, or quantitative physical characterization of the copolymers.

We have studied the copolymerization of vinyl acetate with vinyl palmitate, with vinyl stearate, and with vinyl oleate, and we are reporting (a) a method of preparing and purifying copolymers having a wide range of compositions, (b) proof of copolymerization, (c) determination of monomer reactivity ratios, and (d) physical characterization of the copolymers.

PREPARATION AND PURIFICATION OF COPOLYMERS

Since our previous work on the homopolymerization of the long-chain vinyl esters⁴ showed that solution polymerization produced unbranched and completely soluble polymers, the copolymers were prepared in benzene solution. The polymerization conditions were: ratio of monomer mixture to benzene, 1:2.5 moles; initiator, 0.5 mole per cent benzoyl peroxide based on monomers; temperature, 70–73°C.; time, 7 hours (36 hours for the oleate copolymers); nitrogen atmosphere; reflux condenser to minimize

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TABLE I
COMPOSITION AND CHARACTERISTICS OF COPOLYMERS OF VINYL PALMITATE WITH VINYL ACETATE

Vinyl palmitate in monomer mixture		Copolymer							
Mole %	Weight %	Vinyl Palmitate Weight % ^a	Soluble in ^b	Insoluble in ^b	First-order transition point, °C.				Brittle point, °C.
					Refractometric		Microscopic		
					A ^c	B ^d	A ^e	B ^f	
100	100	100	H	A, M	41.5	39.4	40.2-40.4	33.0	—
75	90.7	89.3	H	A, M	31.2	28.2	31.6	29.0-29.5	—
50	76.6	73.1	H	A, M	28.0	23.5	24.6-25.0	20.0-21.0	—
37.5	66.3	64.5	H, A	M	—	—	—	—	18
25	52.5	49.0	H, A	M	—	14.2	—	—	9
20	45.0	44.2	H, A	M	—	—	—	—	10
17.5	41.0	37.7	H, A	M	—	—	—	—	—
15	36.5	32.8	A	H, M	—	—	—	—	9
12.5	32.0	28.9	A	H, M	—	—	—	—	—
10	26.7	25.5	A	H, M	—	—	—	—	12
5	14.8	14.8	A, M	H	—	—	—	—	22
0	0	0	A, M	H	—	—	—	—	31

^a Based on carbon analysis.

^b H = hexane, A = acetone, M = methanol.

^c Temperature of appearance of first line of demarcation in the field of the refractometer (temperature increasing).

^d Temperature at which an isothermal change in refractive index occurred (temperature decreasing).

^e Temperature of disappearance of double refraction (temperature increasing).

^f Temperature of reappearance of double refraction (temperature decreasing).

^g Reference 9.

TABLE II
COMPOSITION AND CHARACTERISTICS OF COPOLYMERS OF VINYL STEARATE
WITH VINYL ACETATE

Vinyl stearate in monomer mixture		Vinyl stearate weight % ^a	Soluble in ^b	Insoluble in ^b	First-order transition point, °C.			Brittle point ^c °C.
Mole %	Weight %				Copolymer			
					Refractometric	Microscopic		
		A ^c	B ^d	A ^e	B/			
100	100	51.6-51.9	50.0	51.0	48.5-49.5	—		
80	93.4	45.8-46.1	42.0	45.5-46.0	41.0-41.5	—		
50	78.4	40.2-41.0	37.0	40.0-41.0	37.0	—		
33	64.4	38.2-38.5	33.3	—	—	—		
25	54.6	34.0-35.0	29.0	—	—	—		
20	47.4	32.0-33.0	26.0	—	—	20		
15	39.0	—	23.0	—	—	11		
10	28.5	—	—	—	—	12		
5	15.8	—	—	—	—	23		
0	0	—	—	—	—	31		

^a Based on carbon analysis.

^b H = hexane, A = acetone, M = methanol.

^c Temperature of appearance of first line of demarcation in the field of the refractometer (temperature increasing).

^d Temperature at which an isothermal change in refractive index occurred (temperature decreasing).

^e Temperature of disappearance of double refraction (temperature increasing).

^f Temperature of reappearance of double refraction (temperature decreasing).

^g Reference 9.

loss of vinyl acetate; conversion, 55–65% (21–58% for the vinyl oleate copolymers⁴). The compositions of the monomer mixtures are shown in Tables I, II, and III. A more exact technique, described later, was used in the preparation of copolymers for the determination of the monomer reactivity ratios. In the copolymerization of the vinyl esters of the saturated acids, the yield of copolymer in the resulting solution of monomers and copolymers was obtained from a determination of the total solids in the solutions and from an iodine number on the vinyl acetate-free solids. The yields of the vinyl oleate copolymers were determined by evaporating to constant weight an aliquot of a benzene solution of the thrice precipitated copolymer.

After the samples required for the analyses had been removed, the remaining polymer in solution was precipitated by pouring the solution into 5–10 parts by volume of a non-solvent. The precipitation from benzene was repeated twice, and the copolymer was isolated by filtration or decantation and dried at 50°C. in a stream of nitrogen or by the frozen-benzene technique.⁵ The compositions of the copolymers, shown in Tables I, II, and III, were calculated from their carbon content. The degree of polymerization of these copolymers is in the range of 400–500 as determined by light scattering.

TABLE III
COMPOSITION AND CHARACTERISTICS OF COPOLYMERS OF VINYL OLEATE
WITH VINYL ACETATE

Vinyl oleate in monomer mixture		Copolymer				
Mole %	Weight %	Vinyl oleate Weight % ^a	Conversion, %	Soluble in ^b	Insoluble in ^b	Brittle point, °C. ^c
20	47.3	45.1	20.6	A, H	M	–2
10	28.5	28.5	40.5	A, M	H	19
5	15.9	15.9	57.5	A, M	H	22
0	0	0	52.5	A, M	H	31

^a Based on carbon analysis.

^b H = hexane, A = acetone, M = methanol.

^c Reference 9.

PROOF OF COPOLYMERIZATION

That true copolymerization, and not concurrent polymerization of each monomer, had occurred was demonstrated on the basis of solubility. Table I shows the solubility characteristics of the crude (unprecipitated) copolymers of vinyl acetate with vinyl palmitate over a wide range of compositions. Because the copolymers containing up to 82.5 mole per cent vinyl acetate were completely soluble in hexane, a known precipitant for polyvinyl acetate, it was concluded that no polyvinyl acetate was mixed with the copolymers, but that all the vinyl acetate was present as part of the copolymer. Likewise, since the copolymers containing up to 37.5 mole per cent vinyl palmitate were soluble in acetone, a known precipitant for polyvinyl palmitate, it was concluded that no polyvinyl palmitate was present in the copolymers. Therefore, only copolymer is produced when

the monomer mixture is in the range of 17.5 to 37.5 mole per cent vinyl palmitate. In the range above 37.5 mole per cent vinyl palmitate it is possible that polyvinyl palmitate as well as copolymer is produced, and in the range below 17.5 mole per cent it is possible that polyvinyl acetate as well as copolymer is formed. These contingencies, however, are unlikely, since, as will be shown later, the monomer reactivity ratios are nearly the same for both monomers. If copolymerization and concurrent polymerization of each monomer were to occur, it would have to be predicated, therefore, that the rate of copolymerization varies with the starting composition in such a manner that the composition of the polymer always remains approximately the same as the starting composition throughout the entire range of compositions, a highly unlikely situation.

DETERMINATION OF MONOMER REACTIVITY RATIOS

The monomer reactivity ratios for the comonomers vinyl palmitate and vinyl acetate were determined in two ways: the usual, indirect method involving a polymer analysis (Method I), and a direct analysis for each monomer in the reaction solution after polymerization (Method II). Method II was possible because the great difference in vapor pressure between the monomers permitted a quantitative separation of the unpolymerized vinyl acetate by evaporation. Method I gave r_1 (vinyl palmitate) = 0.78 ± 0.10 and r_2 (vinyl acetate) = 1.15 ± 0.13 , and Method II gave $r_1 = 0.66 \pm 0.07$ and $r_2 = 0.84 \pm 0.10$.

The copolymerizations were carried out in benzene (2.5 moles/mole monomer mixture) using 0.5 mole per cent benzoyl peroxide as the initiator at 70–71°C. for two hours in a tube which had been evacuated and then sealed at –70°C. Initial molar ratios of 1:3, 1:1, and 3:1 vinyl palmitate:vinyl acetate were used, and the reactions were performed in triplicate.

At the end of the reaction time the tubes were cooled rapidly, opened, and an amount of hydroquinone equivalent to the benzoyl peroxide originally used was added. Samples of the solutions were then rapidly removed (to minimize evaporation) for the analyses required for Method II. These consisted of determination of total solids and iodine number on the vinyl acetate-free solids. The data obtained are shown in Table IV. From the iodine number, the monomeric vinyl palmitate content was calculated. This value, together with the percentage of total solids and the original monomer composition, permitted a determination of the vinyl acetate and vinyl palmitate content of the copolymers. By difference, the unpolymerized vinyl acetate content was obtained.

The remainder of the benzene solution was diluted with sufficient benzene to produce a solution containing 5 ml. of benzene per gram of monomer mixture, and the polymer was precipitated by pouring the solution into 10 volumes of methanol. The precipitation was repeated twice.⁴ The purified copolymers were dissolved in benzene (10 ml./g.) and the polymer was freed from solvent by the frozen-benzene technique.⁵ Since small amounts of copolymers were present in the methanol-benzene solutions, these were

TABLE IV
DETERMINATION OF MONOMER REACTIVITY RATIOS IN THE COPOLYMERIZATION^a OF VINYL PALMITATE (M_1) WITH VINYL ACETATE (M_2)

Method I					Method II		
(M_1) ^b	(M_2) ^b	(M_1) ^b	(M_2) ^b	Copolymer conversion, %	Analysis C, %	(M_1) ^b	(M_2) ^b
93.1	275.3	70.1	198.5	26.2	66.07	67.1	200.1
93.1	275.3	70.1	200.2	25.9	66.18	67.7	208.5
93.1	275.3	72.9	206.7	23.2	65.97	69.2	209.3
135.6	135.9	91.3	79.6	34.7	70.74	90.7	88.3
135.6	135.9	92.4	85.3	33.1	71.07	92.0	86.9
135.6	135.9	88.0	84.3	35.8	71.38	91.1	85.5
160.6	54.0	96.9	29.3	40.3	74.34	100.6	30.7
160.6	54.0	101.5	31.1	37.4	74.35	103.6	31.4
160.6	54.0	101.5	29.9	37.6	74.24	100.8	29.6

^a 70°C. for 2 hours in 2.5 moles benzene; initiated with 0.5 mole % benzoyl peroxide.

^b Millimoles of unreacted monomer; zero superscript denotes initial quantities.

^c Free from monomeric vinyl acetate.

^d Reference 11.

Total solids ^c		Iodine No. ^d
%		
26.9		51.9
26.3		53.5
26.2		54.9
41.2		54.3
41.2		54.9
41.3		54.2
51.4		53.9
51.4		55.6
51.5		53.9

evaporated to dryness, and the copolymer content was estimated by difference from the weight of the residue and its monomer content (determined by iodine number). The total per cent of monomers which were converted to copolymer was calculated from the weights of the copolymer obtained from the methanol-benzene solutions (a comparatively small amount) and from that obtained by the frozen-benzene technique. The composition of the copolymer, however, was obtained only from the latter. The carbon content of the copolymer was used to determine its composition. Theoretically, the acetyl content of the copolymer should give better precision than the carbon content but we were unable to develop a method for determining the acetyl content with good precision in copolymers with low acetyl contents. The data required for obtaining the monomer reactivity ratios by Method I are given in Table IV.

The monomer reactivity ratios were determined graphically using Mooney's form of the integrated copolymerization equation.⁶ In the estimation of the best values for r_1 and r_2 , the average obtained from all the intersections of each of one series of replicates with each of the other sets was used rather than the circle⁷ or the parallelogram⁸ method. Although the method used is tedious, it is inherently more precise since it does not exclude any values for r_1 and r_2 unless statistical criteria permit such exclusion (in which respect it is more precise than the circle method), and it permits a large number of values close to the mean value to offset the effect of a few values greatly differing from the mean. In the parallelogram method, the least precise experiments determine r_1 and r_2 , and any number of more precise results are without effect.

PHYSICAL CHARACTERIZATION OF THE COPOLYMERS

In a previous paper⁴ we reported the existence of first-order transition points for polyvinyl laurate, myristate, palmitate, and stearate. The copolymers of vinyl acetate with vinyl palmitate and with vinyl stearate containing more than approximately 20-25 mole per cent of the long-chain vinyl ester also exhibit first-order transition points which were determined both refractometrically and microscopically. In the refractometric method the transition temperature was taken as that temperature at which the first line of demarcation appeared in the field of the refractometer as the powdered sample was slowly heated, or as that temperature at which an isothermal change in the refractive index occurred as the sample (in film form) was slowly cooled from above the transition point. The difference existing between these values was ascribed to a hysteresis effect. In the microscopic method, the transition temperature was taken as that temperature at which double refraction disappeared as the sample was slowly heated on the stage of a microscope equipped with polarizing prisms or that temperature at which it reappeared as the sample was cooled. Again a hysteresis effect was noted. The first-order transition temperatures for some copolymers are listed in Tables I and II, and composition-transition temperature plots are shown in Figures 1 and 2. The temperature at which the isothermal change in refractive index occurred was used in Figures 1 and 2.

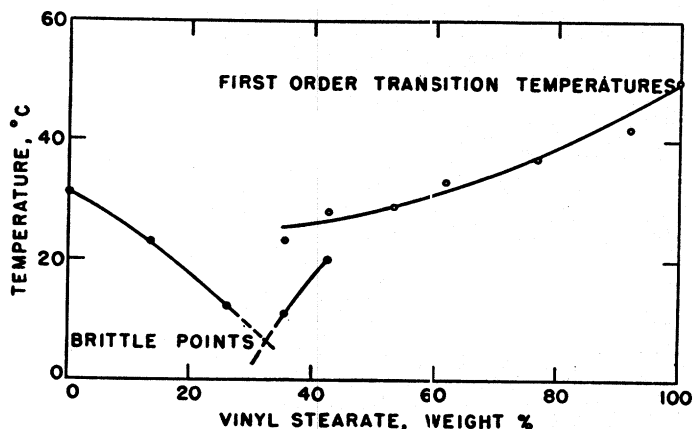


Fig. 1. Physical characteristics of copolymers of vinyl acetate with vinyl stearate. Variation of first-order transition points and brittle points with composition.

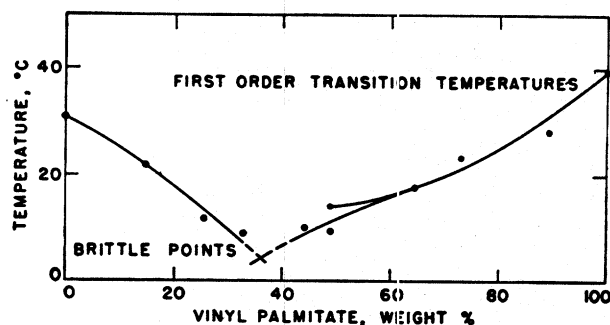


Fig. 2. Physical characteristics of copolymers of vinyl acetate with vinyl palmitate. Variation of first-order transition points and brittle points with composition.

In our previous paper⁴ we reported the existence of first-order transition points in homopolymeric long-chain vinyl esters, a phenomenon which is absent in polyvinyl acetate. Since backbone crystallinity is not known to exist in polyvinyl acetate (the prototype for the long-chain vinyl ester polymers), we ascribed the existence of the first-order transition points in the long-chain polymers to side-chain crystallinity. The evidence offered for this hypothesis was the disappearance of double refraction at the transition temperature, a phenomenon associated with crystallinity. Further evidence for the presence of side-chain crystallinity was found in the investigations of the first-order transition points of the copolymers. If the first-order transition points are due to the orientation of the side chains, some copolymers should also exhibit first-order transition temperatures. Since polyvinyl acetate has no first-order transition point, none should be observed for those copolymers in which the long-chain vinyl ester content of the copolymer has been decreased below a value characteristic for each long-chain vinyl ester. No first-order transition temperatures were found for copolymers containing less than about 20 mole per cent vinyl stearate and 25 mole per cent vinyl palmitate, respectively.

In Figure 3 the data which were obtained in the refractometric determination of the first-order transition temperatures of some vinyl acetate-stearate copolymers are plotted. The isothermal change in the refractive index is clearly visible. In addition it may be seen that the extent of the isothermal change in refractive index decreases as the vinyl stearate content decreases. It would seem logical to suppose that there is some connection between the nature of the crystallinity and the extent of the isothermal change in refractive index, but we have not made a quantitative correlation.

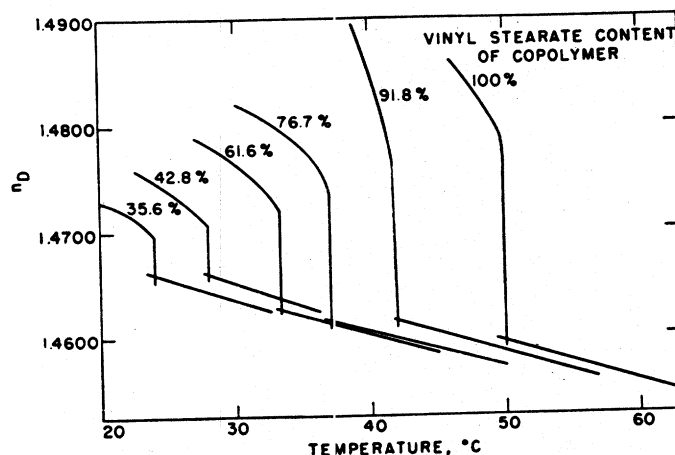


Fig. 3. Determination of first-order transition points of copolymers of vinyl acetate with vinyl stearate. Variation of transition point and refractive index increment at the transition point with composition.

The copolymers which did not have first-order transition points were characterized by brittle points.⁹ These are listed in Tables I, II, and III and the composition-brittle point data are plotted in Figures 1, 2, and 3. It may be seen from the figures that the brittle point passes through a minimum as the vinyl stearate or vinyl palmitate content is varied.

Evaluation of some of the copolymers as adhesives is in progress. Other possible applications which suggest themselves are the formulation of chewing gum bases, coating materials, textile assistants, and as lubricating oil additives.¹⁰

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Synopsis

A study was made of the copolymerization of vinyl acetate with vinyl palmitate, vinyl stearate, and vinyl oleate, respectively. True copolymerization was shown to have occurred on the basis of the solubility characteristics of the crude copolymers over a wide range of compositions. The monomer reactivity ratios for the comonomers vinyl palmitate (r_1) and vinyl acetate (r_2) were determined by two methods. One, based on an analysis of the copolymer, gave $r_1 = 0.78 \pm 0.10$ and $r_2 = 1.15 \pm 0.13$; the other, based on an analysis for each monomer in the mixture remaining after polymerization, gave $r_1 = 0.66 \pm 0.07$ and $r_2 = 0.84 \pm 0.10$. When the vinyl palmitate or vinyl stearate content of the copolymer exceeded about 20–25 mole per cent, the copolymers exhibited first-order transition points which were determined using a refractive index technique as well as a polarizing microscope method. Where no transition point could be observed, brittle point measurements were made.

Résumé

La copolymérisation de l'acétate de vinyle avec le palmitate, le stéarate et l'oléate de vinyle a été étudiée. La copolymérisation est réelle, ainsi qu'il ressort des caractéristiques de solubilité des copolymères bruts, obtenus sur une échelle étendue de composition. Les rapports des réactivités des monomères copolymérisés dans le cas du palmitate et de l'acétate de vinyle (r_1 et r_2) ont été déterminés par deux méthodes. L'une basée sur l'analyse des copolymères indique $r_1: 0.78 \pm 0.10$ et $r_2: 1.15 \pm 0.13$; l'autre méthode, basée sur l'analyse de chaque monomère dans le mélange restant après polymérisation indique $r_1: 0.66 \pm 0.07$ et $r_2: 0.84 \pm 0.10$. Lorsque la teneur en palmitate de vinyle ou de stéarate de vinyle au sein du copolymère dépasse environ 20–25 moles pour cent les copolymères montrent des points de transitions de premier ordre, ainsi qu'ils ont pu être démontré réfractométriquement et au moyen de la méthode au microscope polarisant. Lorsque un point de transition n'a pu être observé, des mesures de points de rupture ont été faites.

Zusammenfassung

Es wurde eine Untersuchung der Copolymerisation von Vinylacetat mit Vinylpalmitat beziehungsweise Vinylstearat und Vinyloleat ausgeführt. Auf Grund der Löslichkeitseigenschaften des rohen Copolymers innerhalb eines grossen Zusammensetzungsbereiches wurde gezeigt, dass wahre Copolymerisation auftrat. Das Monomer-Reaktivitätsverhältnis für die Comonomeren Vinylpalmitat (r_1) und Vinylacetat (r_2) wurde mit zwei Methoden bestimmt. Die eine Methode, die auf der Analyse des Copolymeren begründet ist, ergab $r_1 = 0,78 \pm 0,10$ und $r_2 = 1,15 \pm 0,13$; die andere, die auf der Analyse jedes nach der Polymerisation in dem Gemisch verbleibenden Monomers begründet ist, ergab $r_1 = 0,66 \pm 0,07$ und $r_2 = 0,84 \pm 0,10$. Wenn der Vinylpalmitat- oder Vinylstearatgehalt des Copolymeren ungefähr 20–25 Mol-Prozent überschreitet, zeigen die Copolymeren Umwandlungspunkte erster Ordnung, die sowohl mittels einer Refraktionsindex-Methode, wie auch einer Polarisationsmikroskop-Methode bestimmt wurden. Wo keine Umwandlungspunkte beobachtet werden konnten wurden "brittle point" Bestimmungen ausgeführt.